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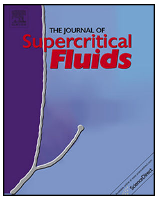

# One-pot supercritical transesterification and partial hydrogenation of soybean oil in the presence of $Pd/Al_2O_3$ or Cu or Ni catalyst without $H_2$

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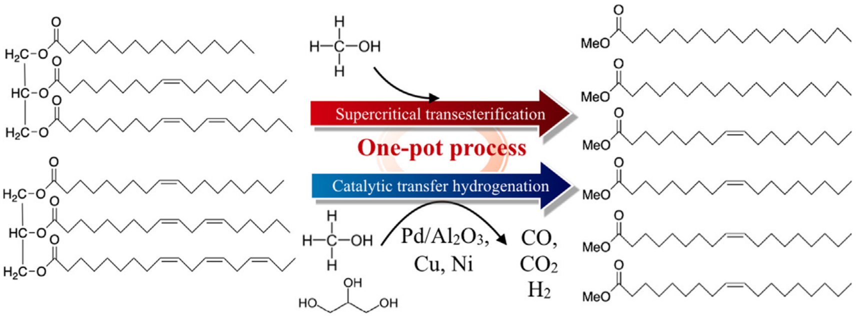
## HIGHLIGHTS

- $Pd/Al_2O_3$, Cu and Ni were active for transesterification and partial hydrogenation.
- Glycerol decomposed and acted as hydrogen donor in the one-pot process like methanol.
- The reduction of a supported catalyst under supercritical methanol was verified.
- Catalysts showed different reactive tendencies according to reaction variables.
- Cu appears to be an appropriate catalyst for the production of methyl oleate.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This study examined a possibility of commercial $Pd/Al_2O_3$, Ni, and Cu as a catalyst for one-pot reaction combining transesterification and partial hydrogenation in supercritical methanol without $H_2$ to produce methyl oleate for bio-refinery or biodiesel with improved fuel quality. The one-pot reaction at different reaction conditions (temperature, pressure, molar ratio of methanol to oil, and reaction time) was conducted to identify the effect of the catalysts and the conditions. Although the one-pot reaction was affected by the catalysts and the conditions, it was inadequate to control the reaction by changing the conditions. Therefore, an attempt to synthesize an appropriate catalyst appears to be essential. Also, decomposition of glycerol and reduction of a catalyst in supercritical methanol were confirmed and verified. Consequently, this result could be helpfull to understand the characteristics of the reaction according to catalysts and conditions and determine a proper metal catalyst for the production of C18:1.

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## 1. Introduction

Fatty acid methyl esters (FAMEs), called as biodiesel, have attracted considerable attention for substituting fossil fuel and reducing the emission of $CO_2$ because it can be made from bio-oil, such as vegetable oil, algae oil, and animal fat, through transesterification with methanol. Among the oils, vegetable oil is the main source for biodiesel because it has the most production all around the world and good cold flow properties due to the high degree of unsaturation [1,2]. Especially, monounsaturated FAMEs such as methyl oleate (C18:1), methyl palmitoleate (C16:1) have been identified as ideal components of biodiesel because of better oxidative

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stability as well as good cold flow properties than highly unsaturated FAMEs [3]. In addition to biodiesel, FAMEs that have a double bond can be utilized to a bio-refinery based on olefin metathesis to produce valuable products like lubricants, surfactants, and polymers [4,5]. C18:1, in particular, is preferred as a model compound for the olefin metathesis because products for the metathesis of C18:1 are simple [6,7]. Also, methyl linoleate (C18:2), and methyl linolenate (C18:3) that could be hydrogenated to C18:1 accounts for a high portion of FAMEs from vegetable oil so that C18:1 can be easily obtained [4]. Therefore, C18:1 is useful and valuable as biodiesel and raw materials for the biorefinery.

For the production of C18:1, vegetable oil with high unsaturation is transesterified to FAMEs and the FAMEs are converted to C18:1 by partial hydrogenation in addition to using vegetable oil with high C18:1, such as camelia oil and olive oil. The reactions for increasing the portion of C18:1 have been usually conducted step by step [8], but a one-pot process combining transesterification and partial hydrogenation was suggested [9,10]. Hempseed oil was used and reacted with methanol at 180 ° under $H_2$ of 3 MPa for 3 h using Cu/SrO. The FAMEs yield of 96 % was achieved and the content of C18:1 was increased from 10.1 % to 46.7 % without the increase of saturated FAMEs, methyl stearate (C18:0). Consequently, the transesterification and the partial hydrogenation has been simplified to one process. Similarly, conversion of unsaturated fatty acid ethyl ester (FAEE) to C18:1 was attempted by simultaneous transesterification and partial hydrogenation at 40 ° under $H_2$ for more than 20 h using a recyclable polymer-supported Pd [11] and fatty acid was also done at 270 ° under $H_2$ for 2 h using $Cu/SiO_2$-$Al_2O_3$ or $SiO_2$-$ZrO_2$ [12]. However, the rate of hydrogenation was so slow that it took a long time to obtain a high portion of C18:1.

Meanwhile, many researchers have paid attention to catalytic transfer hydrogenation (CTH) where hydrogen donor is used instead of $H_2$ gas. This is because it is not required to use explosive $H_2$ gas in CTH. Tetralin [13], isopropanol [8,14], and glycerol [15,16] were used as hydrogen donor with catalysts such as Pd, Ni, Cu, and Co. Like the one-pot process described above, CTH can also be conducted along with transesterification or esterification. Researches for CTH along with transesterification have mainly focused on the conversion of fatty acid and oil to hydrocarbons and alcohol [13–19] and pyrolysis bio-oil to biofuel [20–22], not a preparation of useful C18:1. Also, they did not consider the effect of reaction variables on the reaction and conducted experiments in a limited condition. On the other hand, Shin et al. [23] suggested a simultaneous reaction for partial CTH and transesterification using methanol as a hydrogen donor with Cu powder under supercritical condition. The FAMEs yield of 90 % was achieved and the content of C18:1 was increased from 24.6 % to 54.3 % with the increase of C18:0 of only 2.7 % within 30 min. Even though enrichment of C18:1 was accomplished in the simultaneous reaction without addition of $H_2$ in a brief time, the reaction has been not well understood because the research utilized the only Cu in one condition (320 ° and 20 MPa) and claimed that hydrogen for hydrogenation was donated by decomposition of methanol on Cu. According to previous researches [15,16], it is thought that glycerol that is made from transesterification of oil could be used as a hydrogen donor for the reaction.

Therefore, this study will examine the possibility of $Pd/Al_2O_3$ and Ni which are mostly used for hydrogenation, and oxide forms of Cu and Ni as a catalyst for the one-pot reaction combining transesterification and partial CTH under supercritical methanol in order to concentrate C18:1. Also, a change of an amount of glycerol obtained from the reaction will be identified and the contribution of glycerol and methanol as hydrogen donor will be verified. Furthermore, the effects of reaction variables (temperature, pressure, a molar ratio of methanol to oil, and reaction time) will be investigated according to the catalysts of $Pd/Al_2O_3$, Cu, and Ni. Finally, the fuel properties of FAMEs from the one-pot reaction and characteristics of the catalysts for the reaction will be evaluated.

## 2. Materials and methods

### 2.1. Raw materials

Soybean oil (Beksul, CJ Co., Korea) which has high polyunsaturated fatty acid content was used in this study. Methanol (99.5 %) and n-heptane (99.0 %) were purchased from Samchun Pure Chemical Co. (Seoul, Korea) for reagent and analytic solvent, respectively. Methyl heptadecanoate (C17:0, Sigma-aldrich Co., Seoul, Korea) was used as the internal standard FAMEs for gas chromatography (GC) analysis

Copper (Cu, 99.7 %, Product No. 357456), copper (II) oxide (CuO, 98 %, Product No. 208841), nickel (Ni, 99.7 %, Product No. 266981), nickel (II) oxide (NiO, 99 %, Product No. 399523) were provided by Sigma-aldrich Co. (Seoul, Korea) and commercial palladium-doped alumina ($Pd/Al_2O_3$, 5 % Palladium, Product No.46-1950) was purchased from Stem Chemicals, Inc. (Newburyport, USA). The materials were stored at a desiccator and used without any treatment.

### 2.2. Experimental procedure

A batch-type reactor system was used for the one-pot reaction as described from [24,25]. A stainless steel (SUS 316) reactor with an internal volume of 22 ml was used. Before the reaction, Soybean oil and methanol were injected into the reactor with an amount corresponding to the desired reaction condition based on density data from NIST Chemistry Webbook. After the injection of soybean oil (1.23 g–8.32 g) and methanol (2.03 g–8.47 g), a metal catalyst (123 mg–832 mg) of 10 wt% of the oil was put to the reactor. Subsequently, the reactor was immersed in a preheated molten salt bath containing $KNO_3$, $NaNO_3$, and $Ca(NO_3)_2$ to heat the reactor to the desired temperature. Then, it was shaken horizontally at a frequency of 0.85 Hz for a reaction time using a tailor-made shaker. Before the experiment, the temperature inside the reactor was measured by inserting a thermocouple inside the reactor in advance. The time when the temperature reached the desired value was set to the reaction time of 0 min. After the reaction time, the reactor was rapidly quenched in cool water bath to stop the reaction.

The reaction temperature was set to 250 °, 300 °, and up to 320 ° to avoid thermal decomposition of polyunsaturated fatty acid, such as C18:2, C18:3. Pressure was set at 10 MPa, 20 MPa, and 30 MPa. A molar ratio of methanol to oil was changed from 15:1 to 60:1. An amount of catalyst was fixed at 10 wt% of soybean oil.

Reaction products obtained from the reactor were centrifuged to remove the catalysts from products. After that, residual methanol was evaporated at 80 ° under vacuum for 10 min by using a rotary evaporator. Subsequently, FAMEs and glycerol were separated by centrifugation. The FAMEs were acquired from an upper layer and analyzed by gas chromatography with a flame ionization detector (GC-FID). All of the experiments were performed three times and data from the experiments was documented with the mean average values.

### 2.3. Analysis

#### 2.3.1. Catalyst characterization

The metal catalysts were analyzed by X-ray diffractometer (XRD, JP/D/MAX-2500H, Rigaku Co., Japan) with Cu Kα radiation at 50 kV and 200 mA. A detection angle was from 10° to 90° at a scanning speed of 10°/min. In order to determine a specific surface area and pore size distribution of the catalysts, Brunauer-Emmett-Teller

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